

DEFECTS. DISLOCATIONS. PHYSICS OF STRENGTH**Migration of molecules in *p*-bromochlorobenzene with vacancies in its structure**V. F. Shabanov and M. A. Korshunov¹⁾*L. V. Kirenskiĭ Institute of Physics, Russian Academy of Sciences, Siberian Branch,
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Based on polarization measurements of the low-frequency Raman spectra of *p*-bromochlorobenzene and calculations of the frequency spectra of lattice vibrations by the Dean method it is shown that the structure may contain vacancies. Their presence affects the appearance of additional lines in the low-frequency spectrum, particularly in the vicinity of 70 cm^{-1} , and their positions depend weakly on the orientational disorder of the molecules with respect to the *para* substituents. The activation energies for diffusion in a randomly disordered *p*-bromochlorobenzene crystal with vacancies in the structure is calculated from atom-atom potentials. It is shown that the value of the activation energy varies along a selected direction and depends on the arrangement of the *p*-bromochlorobenzene molecules with respect to the *para* substituents, in contrast to the results for ordered *p*-dibromobenzene and *p*-dichlorobenzene. © 1998 American Institute of Physics. [S1063-7834(98)01410-5]

Low-symmetry organic crystals have become promising materials in molecular electronics, particularly for recording and processing information in optical computers.¹ In practice, crystals whose structure is not described by an ideal three-dimensional lattice are used. The presence of vacancies in the crystal causes the emergence of diffusion. This prevents a reduction in the size of the area needed to record information, since an increase in the recording density depends on the fact that the distance between two light beams passing through a sample can be reduced only as long as independent responses are observed. Gibbs noted in his book² that the occurrence of diffusion can lead to a need for increased separation of the light beams. In addition, a migrating molecule can alter the recorded information. This calls for an investigation of diffusion in molecular crystals.

Low-frequency Raman scattering can be used to determine the presence of vacancies in a crystal (whose presence is responsible for diffusion), since the presence of vacancies in a crystal affects the lattice vibrations and is thus manifested in the spectra.

The manifestations of vacancies in low-frequency spectra have heretofore been studied in molecular crystals consisting of centrosymmetric molecules.³ However, crystals consisting of noncentrosymmetric molecules, such as, for example, *p*-bromochlorobenzene, are often employed in molecular electronics, yet the migration of molecules in a crystal of this compound has not been investigated.

p-Bromochlorobenzene is isomorphous with *p*-dibromobenzene and the α modification of *p*-dichlorobenzene, in which the migration of molecules has been studied.³

According to x-ray structural⁴ and NQR⁵ data, *p*-bromochlorobenzene crystallizes in the centrosymmetric $P2_1/a$ space group with two molecules in the unit cell owing to the statistically disordered arrangement of the mol-

ecules with respect to the *p*-substituted halogen atoms.

The spectrum of lattice vibrations of similar crystals should display six intense lines associated with orientational vibrations and three lines associated with translational vibrations.

The polarization measurements of the spectra of lattice vibrations of *p*-bromochlorobenzene showed that the spectrum contains a series of additional lines, whose intensity does not decrease significantly as the temperature is lowered to 77 K. Table I presents the values of the frequencies of the additional lines of *p*-bromochlorobenzene at room temperature and 77 K. The two lines with frequencies equal to 35 and 60 cm^{-1} at 77 K can be assigned to translational vibrations, in agreement with the data from the IR absorption spectra [36 and 59 cm^{-1} at 80 K (Ref. 6)]. Figure 1a shows the spectrum of *p*-bromochlorobenzene (the *XY* component of the scattering tensor) at 293 K. The additional lines in the spectrum of *p*-bromochlorobenzene can be caused both by the presence of disorder with respect to the *para* positions and the presence of vacancies. Manifestations of vacancies in the spectrum of lattice vibrations can be found by comparing the experimental spectra with spectra obtained from computer calculations with and without consideration of the presence of vacancies in the structure.

In the calculations of the spectra of lattice vibrations, the structure of the molecules was assumed to be absolutely rigid. The interaction between molecules was described by atom-atom potentials.⁷ The coefficients in the interaction potential were the same as in the calculations of the spectra of the frequencies of *p*-dibromobenzene and *p*-dichlorobenzene in Ref. 3.

The spectra of the disordered crystals were calculated by the Dean method.⁸ It permits finding the eigenvalues for

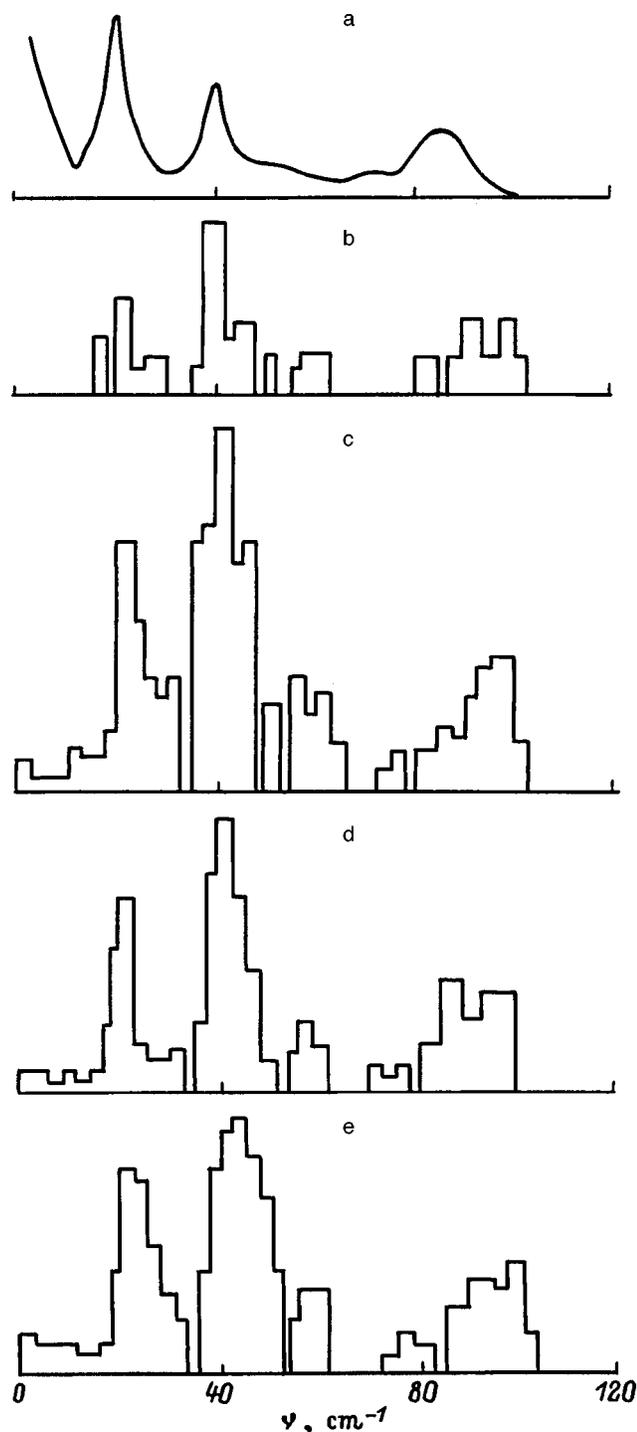


FIG. 1. Experimental low-frequency spectrum of *p*-bromochlorobenzene at 293 K (the *XY* component of the scattering tensor) (a) and histograms obtained from calculations with (c, d, e) and without (b) vacancies in the structure.

high-order matrices. The calculations yielded histograms, which show the probability of the appearance of spectral lines in a selected frequency range.

The histogram of the frequency spectrum of lattice vibrations without vacancies, but with consideration of disorder in the structure with respect to the *para* positions of *p*-bromochlorobenzene is presented in Fig. 1b. As can be

TABLE I. Experimental frequency values (in cm^{-1}) of the additional lines of *p*-bromochlorobenzene at 293 and 77 K.

293 K	77 K
19.5	20.0
-	35.0
-	60.0
72.0	73.0
-	80.0
-	90.0

seen, no lines are observed in the vicinity of 70 cm^{-1} , but additional peaks caused by disorder appear.

The arrangement of the molecules in a crystal lattice with vacancies was found at the free-energy minimum. The minimization was carried out with respect to the orientations and displacements of the centers of gravity of the molecules taken into consideration.

Figure 1c shows the histogram of the spectrum of lattice vibrations of *p*-bromochlorobenzene with vacancies in the structure. As can be seen, additional lines appear in the vicinity of 70 cm^{-1} .

There can be differences in the arrangement of the molecules (with respect to the *para* substituents) surrounding a migrating molecule, which affect the migration energy of the molecule. They can also be reflected in the low-frequency spectra. Figures 1d and 1e show histograms of the spectra of lattice vibrations calculated for two energetically stable arrangements of the molecules. Each of the arrangements is assigned by a dominant arrangement in the structure of the crystal whose histogram is presented in Fig. 1c. As is seen from the histograms, although the positions of the maxima vary somewhat, the lines in the vicinity of 70 cm^{-1} caused by the presence of vacancies in the structure appear in both cases.

Thus, it can be concluded that an unordered crystal of *p*-bromochlorobenzene contains vacancies, which give rise to diffusion in the crystal. The position of the lines in the vicinity of 70 cm^{-1} associated with the presence of vacancies in the structure depends weakly on the orientational disorder of the molecules with respect to the *para* substituents.

Using the same coefficients in the interaction potential as in the calculation of the spectra of lattice vibrations, we calculated the lattice energy, the energy of vacancy formation, and the migration energy of *p*-bromochlorobenzene molecules.

The lattice energy E_L for the molecular arrangement in the structure of *p*-bromochlorobenzene used to obtain the histogram in Fig. 1c is $E_L = 16.7 \text{ kcal/mol}$.

In the calculations of the structure the positions of the vacancies were assigned, and the equilibrium configuration was found. When the molecules relaxed, the energy of *p*-bromochlorobenzene varied by the amount E_R . For the arrangement of molecules chosen it amounts to $E_R = 0.6 \text{ kcal/mol}$. The formation energy of vacancies E_f in this case amounts to $E_f = 16.1 \text{ kcal/mol}$.

When the migration of molecules was considered, a molecule was displaced from the position at (0,0,0) in 0.2-Å steps along a chosen direction toward a vacancy. The energy

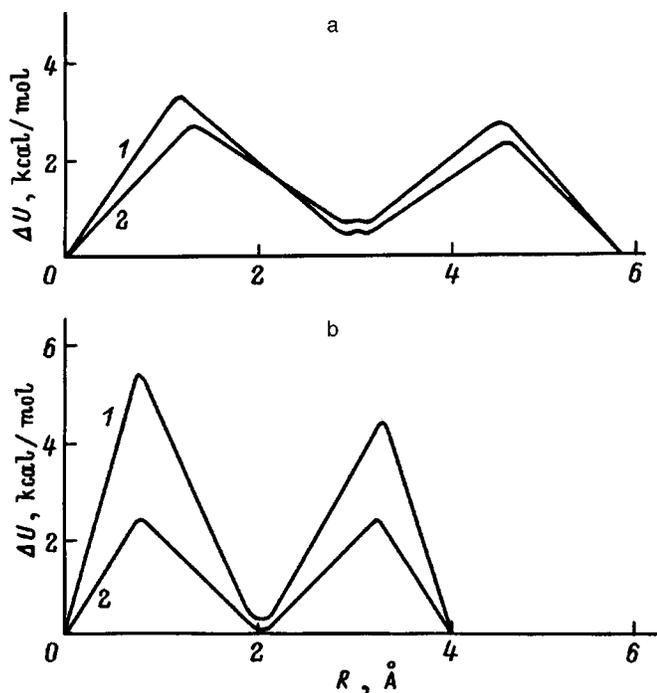


FIG. 2. Variation of the potential energy upon displacement of a migrating *p*-bromochlorobenzene molecule toward a vacancy in the [010] (a) and [001] (b) crystallographic directions: 1—for a disordered (with respect to the *para* positions) arrangement of the surrounding molecules, 2—for an ordered arrangement.

was minimized in each step. Figure 2 presents plots of the variation of the potential energy as a *p*-bromochlorobenzene molecule is displaced along the crystallographic directions [001] (b) and [010] (a).

As a consequence of the different arrangements of *p*-bromochlorobenzene molecules (with respect to the *para* positions), the environment of the migrating molecule is different for different points in the crystal. Depending on the arrangement of the molecules around a vacancy, the plots of the variation of the potential as the molecules are displaced can be either symmetric or asymmetric relative to the middle of the plot. Examples of this are presented in Fig. 2. Curves 1 (in Fig. 2) for the [001] and [010] crystallographic directions are asymmetric. These curves were obtained for one of the possible disordered (with respect to the *para* positions) arrangements of the molecules surrounding the migrating molecule. The curves are asymmetric because the arrangement of the molecules (and their interaction with the migrating molecule) for the point from which the molecule migrates differs from the environment around the point where the vacancy is located. Curves 2 in Fig. 2 were obtained for an ordered arrangement of the molecules.

Thus, it is seen that, unlike the case of ordered *p*-dibromobenzene with centrosymmetric molecules, the value of the migration energy can differ from cell to cell for the same migrating molecule.

In the cases considered the migration energy along the [010] crystallographic direction has the values $E_{m1}^{[010]} = 3.3$ kcal/mol and $E_{m2}^{[010]} = 2.8$ kcal/mol. The positions of the maxima (along the horizontal axis) for them are different.

After passing the maximum on curves 2, there is sharper variation of the orientation of the migrating molecule. The angle between the planes of the undisplaced and displaced molecules after passage of the maximum equals about 60° in all the cases considered.

The migration energy of *p*-bromochlorobenzene molecules along the [001] crystallographic direction has the values $E_{m1}^{[001]} = 5.5$ kcal/mol and $E_{m2}^{[001]} = 2.5$ kcal/mol in the cases considered. The positions of the maxima for both cases scarcely changed.

The results of the calculations of the activation energy show that its value also varies. The values for the [010] crystallographic direction are $E_{d1}^{[010]} = 19.4$ kcal/mol and $E_{d2}^{[010]} = 18.9$ kcal/mol. In the [001] direction the values are $E_{d1}^{[001]} = 21.6$ kcal/mol and $E_{d2}^{[001]} = 18.6$ kcal/mol, respectively.

Therefore, unlike centrosymmetric *p*-dibromobenzene, whose activation energy is larger along the [001] crystallographic direction than along the [010] direction, in *p*-bromochlorobenzene the activation energy can vary as a function of the arrangement of the molecules with respect to the *para* substituents. In this case variation of the direction of diffusion from cell to cell is possible [either the molecule can migrate along the (001) or (010) direction, or the directions are equally preferable]. Apparently, when the experimental results on the activation energy in *p*-bromochlorobenzene are compared with the calculated values, the averaged values of the energy along the respective direction should be considered.

Thus, it has been shown that there are vacancies in the structure of *p*-bromochlorobenzene. Their presence affects the appearance of the additional lines in the vicinity of 70 cm^{-1} in the spectrum of lattice vibrations, in agreement with the data on *p*-dibromobenzene and *p*-dichlorobenzene. The positions of the lines in the vicinity of 70 cm^{-1} depend weakly on the orientational disorder of the molecules with respect to the *para* substituents. Calculations of the activation energy in *p*-bromochlorobenzene have shown that, in contrast to the case of *p*-dibromobenzene, it is not a constant along the crystallographic direction selected, but depends on the arrangement of the *p*-bromochlorobenzene molecules with respect to the *para* substituents.

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